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Penetration-resistant material and articles made of the same

Description:

The invention pertains to a penetration-resistant material and to articles made of the same.

Penetration-resistant articles such as bulletproof vests, helmets, vehicle panels and shields prepared from high strength fibers are known in the art. For many applications, in particular for ballistic vests, the fibers are used in a woven or knitted fabric. This fabrics may be coated or impregnated in a matrix to obtain hard ballistic materials, or may be used free from matrix to obtain soft ballistic materials.

Bulletproof fabrics are known, inter alia, from EP 310 199. The fabrics disclosed therein are composed of filament yarns of ultrahigh molecular weight polymer having high strength and high modulus, with the warp threads being of a different polymeric material than the weft threads.

In Russian Patent RU 2 096 542 a ballistic fabric for bulletproof jackets was disclosed having warp and weft threads of poly para-phenyleneterephthalamide (PPTA) wherein the ratio of the warp to the weft linear density is smaller than 4.17. Typically, warp threads having a linear density of 143 to 588 dtex and weft threads having a linear density of 588 to 930 were disclosed, the weft threads having equal or higher linear density than the warp threads. It is particularly contended that ballistic fabrics having warp to weft linear density ratios between 1.59 and 4.17 have improved deflection properties.

In WO 00/42246 a penetration-resistant material is disclosed comprising at least a double layer of fabric composed of two layers of woven fabric which are cross-plied at an angle wherein the fabric is composed of a first set of threads comprising 3.5 to 20 threads/cm and having a linear density of at least 420 dtex, and a second set of threads comprising 0.5 to 8 threads/cm and having a linear density of at least 50 dtex, with the second set of threads being transverse to the first set of threads and wherein the ration of the linear density of the first set of threads to the linear density of the second set of threads is > 4.2, more preferably > 7.5. In a preferred embodiment the first set of threads is warp threads made of p-aramid yarn and the second set of threads ist weft threads made of polyester yarn, and the ratio of the number of threads/cm of the first set to that of the second set is > 1. Although the ballistic performance of this material is excellent, the necessity of cross-plying the layers is a disadvantage in terms of ease and simplicity of the manufacture and the danger of creating weak points that inherently to the process of cross-plying can occur.

So, the problem underlying the present invention is to provide a penetration-resistant material which does not exhibit the disadvantages of the prior art.

Some penetration-resistant materials exhibit a high uptake of water resulting in a decrease of ballistic performance. Therefore, another problem underlying the present invention is to reduce this drawback.

These problems are solved by a penetration-resistant material comprising at least a double layer of woven fabric wherein the double layer comprises a first layer of fabric composed of a first set of threads comprising 3.5 to 20 threads/cm, having a linear density of at least 210 dtex, and comprising at least 65 % of the fabric weight, and a second set of threads comprising 0.5 to 16 threads/cm and having a linear density of at least 50 dtex, with the second set of threads being transverse to the first set of threads, and the ratio of the number of threads/cm of the first set to that of the second set is > 1, and a second layer of fabric composed of a first set of threads comprising 0.5 to 16 threads/cm and having a linear density of at least 50 dtex, and a se-

second set of threads comprising 3.5 to 20 threads/cm, having a linear density of at least 210 dtex, and comprising at least 65 % of the fabric weight, with the second set of threads being transverse to the first set of threads, and the ratio of the number of threads/cm of the second set to that of the first set is > 1, and wherein the first and second sets of threads of the first layer have a parallel orientation towards the first and second sets, respectively, of threads of the second layer, which penetration-resistant material is characterized in that in the first layer of fabric at least the first set of threads and in the second layer of fabric at least the second set of threads are treated with a water-repellant.

Within the scope of the present invention the term „thread" means any sort of thread such as staple yarn, twisted staple yarn, twisted filament yarn, non-twisted intermingled yarn, and preferably, untwisted filament yarn.

In a preferred embodiment of the penetration-resistant material according to the present invention in the first layer of fabric the first and the second set of threads and in the second layer of fabric the first and the second set of threads are treated with a water-repellant.

Within the scope of the present invention in principle any substance which repells water and which can be applied to the threads with known methods can be used as the water-repellant. However, because of it's high water-repellant efficiency a water-repellant comprising fluor and carbon atoms, e.g. a fluoropolymer, and especially a mixture of fluoroacrylate polymers, is preferred. Said mixture is for example contained in OLEOPHOBOL SM® from Ciba Spezialitätenchemie Pfersee GmbH, Langweid am Lech, DE.

In a preferred embodiment of the penetration-resistant material according to the present invention the water-repellant treated threads comprise about 0.1 to about 2 weight % flouroacrylate polymers with respect to the weight of the water-repellant

treated threads. Especially preferred is about 1 weight % fluoroacrylate polymers with respect to the weight of the water-repellant treated threads.

Preferably, in the penetration-resistant material according to the present invention at least the ratio of the linear density of the first set of threads to the linear density of the second set of threads of the first layer and of the linear density of the second set of threads to the linear density of the first set of threads of the second layer is > 1, more preferably > 4.2 and most preferably > 5.9. A particular effective ratio is 6 - 6.6.

In a preferred embodiment of the penetration-resistant material according to the present invention at least one of the second set of threads of the first layer and the first set of threads of the second layer comprises 0.5 to 8 threads/cm.

In each layer the threads having a linear density of at least 210 dtex comprise at least 65 % of the fabric weight of that layer. Preferably, these threads comprise at least 70 % and more preferably 75 % of the fabric weight of that layer.

The second set of threads is transverse to the first set of threads in each of the two layers. Usually these sets are about perpendicular to each another, but this is not necessary. The second set of threads may be provided under an angle other than 90° to the first set of threads. The two layers are secured together without cross-plying.

In a preferred embodiment of the penetration-resistant material according to the present invention the threads of the layers of the double layer are bonded together, for instance, by stich bonding, or preferably with an adhesive material. The adhesive material may be adhesive material provided onto the threads or onto the fabric, for instance as a finish.

The adhesive material can also be an adhesive layer provided between the two fabric layers of the double layer.

Adhesive materials include

- thermoplastic materials, for example polyolefins such as polyethylene and polypropylene, polyamide, polyester or mixtures of these materials,
- elastomeric materials, for example Kraton, rubber, silicon and the like and
- thermoset materials, for example epoxy resins, polyester resins, phenolic resins, vinylester resins and the like.

It is also possible to use for at least part of the second set of threads of the first layer and the first set of threads of the second layer a material that melts under pressure and/or heating, thereby accomplishing binding the threads of the first set, respectively second set of threads to those of the second set, respectiveley first set of threads, and optionally also binding the two fabric layers together.

The number of threads per cm in the first set of threads of the first layer and the second set of threads of the second layer is 3.5 to 20 threads/cm, more preferably 4 to 15 threads/cm and most preferably 5 to 12 threads/cm.

The number of threads per cm in the second set of threads of the first layer and the first set of threads of the second layer is 0.5 to 16 threads/cm, preferably 0.5 to 8 threads/cm, more preferably 1 to 6 threads/cm and most preferably 2 to 4 threads/cm.

The first set of threads of the first layer (preferably warp threads) and the second set of threads of the second layer (preferably weft threads) are of high strength and high modulus.

In a preferred embodiment of the penetration-resistant material according to the present invention the first set of threads of the first layer and the second set of threads of the second layer consist of high tenacity threads selected from aramid, polyethylene and poly-p-phenylenebenzobisoxazole (PBO) threads, whereby for the aramide more

particularly p-aramid threads and most preferred poly paraphenyleneterephthalamide (PPTA) is used, for example Twaron® threads manufactured by Teijin Twaron.

The penetration-resistant material according to the present invention also consists of a second set of threads of the first layer (preferably weft threads) and a first set of threads of the second layer (preferably warp threads), the yarn composition of which is not decisive for the present invention. Preferably, however, these threads exhibit a high strength and a high modulus. This is particularly the case when the second set of threads of the first layer and the first set of threads of the second layer are selected from polyester, polyethylene, polypropylene and aramid threads, for example Twaron® threads manufactured by Teijin Twaron. Most preferably, the second set of threads of the first layer and the first set of threads of the second layer is made of polyester thread.

In a peferred embodiment of the penetration-resistant material according to the present invention the warp and the weft threads are selected to be made of different polymers, for instance a fabric having warp threads of p-aramid yarn and weft threads of polyester yarn, or reversed, is preferred. An example for such a preferred embodiment is a penetration-resistant material wherein the first set of threads of the first layer and the second set of threads of the second layer consist of aramid threads, and the second set of threads of the first layer and the first set of threads of the second layer consist of polyester threads.

As long as the required linear density ratio is satisfied, the linear density of the first set of threads of the first layer and of the second set of threads of the second layer is selected to be at least about 210 dtex, preferably between 210 and 6720 dtex, more preferably between 420 and 3360 dtex, even more preferable between 420 and 1680 dtex and most preferably between 840 and 1100 dtex.

The linear density of the second set of threads of the first layer and the first set of threads of the second layer is at least 50 dtex. In a preferred embodiment of the pe-

netration-resistant material according to the present invention the linear density of the second set of threads of the first layer and of the first set of threads of the second layer is between about 50 and 280 dtex and most preferably between 80 and 140 dtex.

For reasons of efficient manufacturing of the penetration-resistant material according to the present invention it is preferred that the first set of threads of the first layer and the first set of threads of the second layer are warp threads and the second set of threads of the first layer and the second set of threads of the second layer are weft threads.

In a peferred embodiment of the penetration-resistant material according to the present invention the double layer exibits two outer sides and at least one of the outer sides of the double layer is provided with a protective layer which can be a thermoplastic, thermoset or an elastomeric material or a mixture of these materials. The protective layer is applied to protect the fabric from damage by excessive abrasion and to improve the ballistic performance.

The penetration-resistant material according to the present invention comprises at least one double layer consisting of two layers of woven fabric, which are non-cross-plied and optionally bonded together. The term „woven" includes all types of weaves, such as plain weave, satin weave, basket weave, twill weave and the like. Preferred fabrics are plain woven.

The penetration-resistant material according to the present invention may contain as little as one double layer consisting of two layers of woven fabric, but usually more double layers are applied. Suitable numbers of double layers are 5 to 100. Most preferably 6 to 35 double layers are used. The first set of threads of the first fabric layer of a double layer may be parallel to, or at an angle to the first set of threads of the first fabric layer of the adjacent double layer. If these sets are secured together under an angle, such an angle is preferably 90°.

As mentioned before, the double layers may be secured together using an adhesive layer or by stiching. Such adhesive layer may be made of the previously mentioned adhesive materials and has a thickness between 4 and 36 µm, preferably between 8 and 20 µm.

Methods of manufacture of the double layers are well known in the art. Usually the fabric is made by warping the warp yarn on a beam, followed by weaving on a loom. The single layer may optionally be impregnated or laminated and be subjected to a calendering or lamination process. At least two fabric layers can be bonded together by stiching, heating or applying pressure.

The invention pertains also to an article made of the penetration-resistant material of the present invention according to the methods known to the skilled man. Examples for such an article are bullet proof vests and armor plates.

The invention is further illustrated with the following examples.

Example

A penetration-resistant material containing 22 double layers was manufactured by the following procedure.

The first layer of each double layer was produced from Twaron® 930 dtex ex Teijin Twaron in warp direction (9.5 threads/cm, water-repellant treated with OLEOPHOBOL SM® ex Ciba Spezialitätenchemie Pfersee GmbH, Langweid am Lech, DE) and polyester 140 dtex (Trevira® 710, ex Hoechst) in weft direction (2 threads/cm).

The second layer of each double layer was produced from polyester 140 dtex (Trevira® 710, ex Hoechst) in warp direction (4 threads/cm) and Twaron® 930 dtex ex Teijin Twaron in weft direction (9.5 threads/cm, water-repellant treated with OLEOPHOBOL

SM® ex Ciba Spezialitätenchemie Pfersee GmbH, Langweid am Lech, DE). The warp/weft ratio of the first layer and the weft/warp ratio of the second layer was 6.6.

To prepare a double layer the first and second layer were laminated together with 3 plies of a polyethylene film (LDPE, ex EKB) having a thickness of 10 µm, one sheet of polyethylene film being placed on both outer sides of the double layer and one sheet of polyethylene film being placed in-between each of the two fabric layers of the double layer. 22 double layers were prepared in this way.

Said 22 double layers separated from each other by a release paper were superimposed, placed in a press and pressed at a temperature of 120 °C and at a pressure of 25 bar during 25 minutes. Then, the heating of the press was switched of. Afterwards, the 22 double layers were seperated from each another, the release paper was removed, and the 22 double layers were superimposed again to result in a penetration resistant material with a weight of about 4730 g/m².

Comparative example

A penetration-resistant material with a weight of about 4730 g/m² was manufactured as in the example with the only difference that none of the threads were water-repellant treated.

v_{50} - determination

v_{50} - values were determined with 9 x 19 Para type DM 11 A1B2 DAG bullets, wherein v_{50} is the velocity at which 50 % of the bullets are stopped and 50 % of the bullets give full penetration. The penetration resistant material subjected to the v_{50} - determination was in the dry state. That means that said material was tested at room temperature and at a relative humidity of about 60 %.

With each penetration-resistant material two v_{50} measurements were performed the results of which were averaged as shown in the following table.

Penetration-resistant material of	v_{50} (m/s) 1st measurement	v_{50} (m/s) 2nd measurement	v_{50} (m/s) averaged
example	496	505	501
comparative example	483	492	488

The table shows that the penetration-resistant material of the example exhibits an averaged v_{50} - value which is 2.7 % higher than that of the penetration-resistant material of the comparative example. Said difference in v_{50} corresponds to a 5.4 % higher energy absorption of the penetration-resistant material of the example if compared with the penetration-resistant material of the comparative example without any water-repellant treated threads.

Bundesmann rain-shower test

The penetration-resistant materials according to the example and the comparative example were subjected to the Bundesmann rain-shower test (ISO 9865). The following table shows the weight percentage of water uptake after 10 minutes.

Penetration-resistant material of	weight % water uptake
example	10.5
comparative example	34.4

The table shows that the penetration-resistant material of the example exhibits a water uptake which is only about a third of the water uptake of the penetration-resistant material of the comparative example without any water-repellant treated threads.